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1 Stochastic evaluation of annual micropollutant loads and 2 their uncertainties in separate storm sewers

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13 14 **Abstract:**

15 This article describes a stochastic method to calculate the annual pollutant loads and its
16 application over several years at the outlet of three catchments drained by separate storm
17 sewers. A stochastic methodology using Monte Carlo simulations is proposed for assessing
18 annual pollutant load, as well as the associated uncertainties, from a few event sampling
19 campaigns and/or continuous turbidity measurements (representative of the Total Suspended
20 Solids concentration (TSS)). Indeed, in the latter case, the proposed method takes into account
21 the correlation between pollutants and TSS. The developed method was applied to data
22 acquired within the French research project “INOGEV” (Innovations for a sustainable
23 management of urban water) at the outlet of three urban catchments drained by separate storm
24 sewers. Ten or so event sampling campaigns for a large range of pollutants (46 pollutants and
25 2 conventional water quality parameters: TSS and total organic carbon (TOC)) are combined
26 with hundreds of rainfall events for which, at least one among three continuously monitored
27 parameters (rainfall intensity, flow rate and turbidity) is available.

28 Results obtained for the three catchments show that the annual pollutant loads can be
29 estimated with uncertainties ranging from 10% to 60%, and the added value of turbidity
30 monitoring for lowering the uncertainty is demonstrated. A low inter-annual and inter-site
31 variability of pollutant loads, for many of studied pollutants, is observed with respect to the
32 estimated uncertainties, and can be explained mainly by annual precipitation.

33
34 **Keywords:** Stormwater; database; pollutant; annual load; turbidity; TSS; uncertainties;
35 variability.

36

37 INTRODUCTION

38 In the case of separate storm sewers, runoff is usually discharged directly into the natural
39 environment without any treatment. These discharges constitute a continuous and significant
40 vector of pollutants towards receiving waters (Becouze-Lareure et al. 2011, Clark et al. 2007,
41 Weiss et al. 2008, Zgheib et al. 2012). The reduction of these discharges is a major issue of
42 the EU Water Framework Directive (WFD) (2013/39/EU) to achieve the “good ecological
43 status” for all of Europe's surface waters and groundwater. This challenge requires accurate
44 knowledge of pollutant loads discharged by separate sewer. Beyond the conventional water
45 quality parameters (Total Suspended Solids (TSS); Chemical Oxygen Demand (COD); etc.)
46 extensively studied over several decades, monitoring of priority and/or emerging substances
47 has become an important issue in Europe to meet the requirements of the WFD (Sebastian et
48 al. 2011). Due to financial costs, operational and technical issues, the assessment of pollutant
49 loads is constrained by a lack of suitable measuring devices. Monitoring is frequently carried
50 out by taking samples for subsequent analysis in the laboratory. Analytical methods are
51 standardized but still pollutant dependant. Yet, the sampling process has some major
52 drawbacks, among which the limited number of samples which can practically be handled due
53 to random occurrence of rain events, frequent maintenance, etc. Indeed, monitoring programs
54 prove to be very costly and require considerable staff time. Only a limited number of
55 campaigns (generally less than 5) are thus carried out during a given year (Gromaire et al.
56 2007) for operational purposes, and data are usually pooled to derive an Annual (or Site-
57 specific) discharge-weighted (or arithmetic) Mean Concentration SMC, whose value is then
58 multiplied by the total runoff volume of the considered period to assess pollutant loads. This
59 method induces large uncertainty values (Mourad et al. 2005).

60
61 Besides these considerations TSS have been revealed as the predominant pollutant vector in
62 sewer systems (Ashley et al. 2005, Zgheib et al. 2012). In fact, for some pollutants such as
63 PAH, PCB and metals, TSS is a significant vector, while isn't for other pollutants such as
64 Octylphenol OP, TSS is not the significant vector (Zgheib et al. 2012).

65
66 Continuous turbidity measurements can now provide recordings which are representative of
67 the TSS concentration. Actually, turbidity can be translated into TSS concentration by using
68 an average TSS-Turbidity relationship at different time-scales (Hannouche et al. 2011, Lacour
69 et al. 2009, Langeveld et al. 2005, Metadier and Bertrand-Krajewski 2012). TSS
70 concentration time-series are thus made available. The use of continuous measurement data
71 (rain intensity, flow rate, turbidity), in addition to a limited number of laboratory analysis by
72 sampling, therefore enables a more accurate assessment of the annual micropollutants flux.

73
74 In this context, the “INOGEV” project (*Innovations for a sustainable management of urban*
75 *water*) was launched in early 2010 by the national network of French observatories in urban
76 hydrology “SOERE URBIS” (*A long-term Observation System for research and*
77 *Experimentation on urban environment*) combining the works of “OPUR” in Paris
78 (*Observatory of Urban Pollutants in Île-de- France/Paris region, since 1994*), “OTHU” in
79 Lyon (*Field Observatory for Urban Water Management in Lyon-France, since 1999*) and
80 “ONEVU” in Nantes (*Observatory of urban environments of Nantes- France, since 2006*).
81 This project aimed at improving the knowledge and control of the contamination of urban
82 stormwater in a multidisciplinary approach as regards scientific research, operational practices
83 and social understanding. By harmonizing scientific approaches and monitoring
84 methodologies (pollutants, sampling, analytical methods and results interpretation) at the
85 scale of three urban districts featuring distinct land use patterns and contexts, a new extended

86 French dataset has been built for a large range of pollutants at the event scale (Gasperi et al.
 87 2014). In addition, the observatories had formerly provided some statistically representative
 88 databases for water flow rate and turbidity measurements for several years at the outlet of two
 89 of the three studied catchments.

90
 91 In this paper, a combined approach was adopted coupling the new dataset of pollutant
 92 concentrations and available recordings of hydrological and water quality parameters (rainfall
 93 intensity, flow rate, turbidity), to assess annual pollutant loads as well as the associated
 94 uncertainties. First the databases used are briefly presented. Then, the methodology developed
 95 to assess the annual loads and their uncertainty for a given pollutant including the underlying
 96 hypotheses is described. Results obtained are then discussed and compared between the three
 97 sites.

98 **EXPERIMENTAL DATA**

99 **Sites description**

100 Three experimental sites drained by a separate sewer systems (*Sucy* in Île-De-France/Paris
 101 region, *Chassieu* in Lyon and *Pin Sec* in Nantes) were considered. *Table 1* summarizes the
 102 main characteristics and the available databases at the three sites. Their areas range from 30 to
 103 228 ha and their runoff coefficients (*RC*) vary between 22 (*Sucy*) to 30% (*Chassieu*).
 104 *Chassieu* is an industrial catchment while other catchments are residential with mostly small
 105 private houses and limited commercial and professional activity (small shops and services) at
 106 *Sucy* catchment, and mainly collective buildings and private houses at *Pin Sec* catchment. On
 107 the whole, most of buildings and houses were built between the years 1970 and 1980.

108
 109 **Table 1: Sites and databases available**

Sites	Location	Area	RC ¹	Land use	Slope	Available data
<i>Sucy</i>	Paris, South- East	228 ha	0.22	Residential	0.2%	- Continuous rainfall intensity, flow and turbidity measurements (Time step=2 min; 2011-2012): 121/220 rain events ^(2, a) ; - Sampled rainfall events ⁽³⁾ : 24 (7-10 ⁽⁴⁾)
<i>Chassieu</i>	Lyon, East	185 ha	0.30	Industrial	0.4%	- Continuous rainfall intensity, flow and turbidity measurements (Time step=2 min; 2004-2008): 263/655 rain events ^(2, a) ; - Sampled rainfall events ⁽³⁾ : 7 (2-5 ⁽⁴⁾)
<i>Pin Sec</i>	Nantes, North- East	30 ha	0.26	Residential and collective housing	1.0%	- Continuous rain intensity and flow measurements (Time step=5 min; 2011-2012): 198/214 rain events (2, b); - Sampled rainfall events (3): 18 (7-15 (4))

110 (1) *RC* = runoff coefficient (see Precipitation – volume model (Model M1) for more information), (2) number of rainfall
 111 events with: (a), valid flow and turbidity measurements compared to all identified rain events, (b) valid flow
 112 measurements compared to all identified rain events (no turbidity measurement at *Pin Sec* site); (3) Number of rainfall
 113 events sampled at each site with measurements of global parameters; (4) Number of rain events analyzed for each group
 114 of micropollutants.

115 **Available monitoring data**

116 **Sampled rainfall events and measured pollutants**

117 Depending on the site under consideration, between 7 and 24 rainfall events were sampled
 118 from July 2011 to May 2013 with automatic samplers controlled by a flow-meter to obtain
 119 flow proportional event mean concentrations (EMC). The sampling equipment and field blank
 120 procedures were harmonized between observatories and described in (Gasperi et al. 2014).

121

122 The main characteristics of these events such as precipitation depth (H in mm), mean and max
123 intensity in 5 min (I_{mean} and I_{max} in $mm.h^{-1}$) and preceding dry weather period (PDWP in days)
124 are given in *Table 6* in supplementary materials section. On the whole, these rainfall events
125 feature relatively low rainfall intensities, with no extreme rainfall amounts collected.

126
127 Conventional water quality parameters, such as TSS and total dissolved and particulate
128 organic carbon (TOC, DOC and POC), were analyzed for each rain event sampled. A total of
129 46 micropollutants were monitored for 2 to 15 rainfall events, including 13 metals, 16
130 polycyclic aromatic hydrocarbons (PAH), 9 polybromodiphenylethers (PBDE), bisphenol A
131 (BPA) and 7 alkylphenols (APnEOs). The full list of targeted molecules and the usual
132 abbreviations are listed extensively in *Table 7* supplementary materials section.

133 **Continuous measurements**

134 All sites are equipped with monitoring stations for rainfall intensity, flow rate. Rainfall
135 intensities at each catchment area were measured by tipping bucket rain gauges. Raw data
136 were converted into 5 min time step time series. The flow rates are derived from both water
137 level and flow velocity monitoring at the outlet of each catchment. Turbidity was monitored
138 continuously at *Sucy* and *Chassieu*, with two redundant turbidity sensors at a 2 min time step:

- 139 - In *Sucy* site, 2 turbidimeters (Ponselle brand, TU-TRANS-NA) with attenuation at 880 nm
140 and calibration using formazin (range=0-2000 FAU (Formazin Attenuation Unit)) are
141 used. The sensors are installed in the storm sewer pipe, next to the point of flow
142 measurement.
- 143 - In *Chassieu* site, 2 turbidimeters (one Endress-Hauser W CUS31 and one Dr Lange
144 Solitax) with nephelometry at 860 nm and calibration using Formazin (range =0-4000
145 FNU (Formazin Nephelometry Unit)) are used. The turbidity is measured in an off-line
146 monitoring flume installed in a shelter located above ground (Metadier and Bertrand-
147 Krajewski 2012). Water is pumped from the sewer into the flume by a peristaltic pump at
148 approximately 1 L/s and a suction velocity of approximately 1 m/s to avoid settling and
149 particle segregation in the pumping tube.

150
151 Turbidity data were processed and validated by using redundancy in *Sucy* (Lacour et al. 2009)
152 site or by using the method detailed in (Mourad and Bertrand-Kralewski 2002) in *Chassieu*
153 site.

154
155 Storm events are identified using flow rate and rainfall intensity. The beginning of the event is
156 given by the rise of the flow rate signal whereas the end of the event is given by the return to
157 the dry weather base-flow attributed to groundwater infiltration. In a second step, the runoff
158 events identified are compared to rainfall data to eliminate all hydrographs which correspond
159 to a precipitation depth lower than $0.5 mm$ ($<$ Initial loss, see Precipitation – volume model
160 (Model M1) for more information). During the years 2011 and 2012: i) 220 rain events have
161 been identified for *Sucy* site including 121 rainfall events with valid flow and turbidity
162 measurements, ii) and 214 rain events for *Pin Sec* site among which 198 events possess valid
163 flow measurements). Over the period 2004–2008 in *Chassieu* site, the final validated database
164 (flow and turbidity) contains 263 events among 655 identified rain events (*Table 1*). Indeed,
165 data acquired at this site between 2011 and 2012 was not exploitable because of the failures of
166 the peristaltic pump.

167
168 The main characteristics of these rainfall events are given in *Table 2*. The characteristics of
169 these rainfall events are with the same magnitude as those sampled during the pollutant
170 sampling campaigns.

171
172

Table 2: Main rainfall characteristics of the identified rain events on the three study sites (d₁₀-d₅₀-d₉₀).

	H (mm) ⁽¹⁾	Duration (h)	I _{mean} (mm.h ⁻¹)	I _{max} (mm.h ⁻¹) ⁽²⁾	PDWP ⁽³⁾
<i>Sucy</i> (n=121)	1.4-5.0-12.7	1.0-4.7-13.0	0.6-1.3-2.7	2.4-4.8-21.6	0.22-1.29-5.12
<i>Chassieu</i> (n=263)	1.0-2.4-14.7	0.7-3.5-13.0	0.3-1.1-2.8	1.5-4.4-17.5	0.25-0.65-5.6
<i>Pin Sec</i> (n=198)	1.3-3.2-13.0	0.7-2.2-11.8	0.8-2.2-3.6	3.1-7.3-15.5	0.11-0.97-9.54

1) Precipitation depth; 2) I_{max} evaluated over 5-min intervals; 3) Preceding dry weather period, in days.

173 TSS-Turbidity correlation functions and uncertainties

174 Previous research demonstrated that linear or polynomial function can be used to estimate
175 TSS concentration from turbidity (Hannouche et al. 2011, Metadier and Bertrand-Krajewski
176 2012).

177 For *Sucy*, the discharge-weighted event mean turbidity (EMT) was calculated from the
178 continuous and validated turbidity measurements for 14 rainfall events among the 24 rainfall
179 events sampled in *Sucy* site. The 14 pairs (EMT, TSS) obtained allowed us to build the TSS-
180 turbidity linear function (*Figure 1*, (a); $TSS_{(mg/l)}=f(EMT_{(FAU)})=31.9+0.45EMT$, (Equation 1))
181 at the event scale. For each rainfall event *j* for which there is a validated turbidity
182 pollutograph (T_{ij}) (*i* is an index of the time step) and flow rate hydrograph (Q_{ij}), a discharge-

183 weighted event mean turbidity is calculated $T_j \approx \frac{\sum_{i=1}^{n_j} T_{ji} \times Q_{ji} \times \Delta t_{ji}}{\sum_{i=1}^{n_j} Q_{ji} \times \Delta t_{ji}}$ (Equation 2) and then

184 transformed into TSS event mass by applying the TSS-turbidity linear function established on
185 this site. Finally, the residual error implied by this conversion is assessed by assuming that
186 residual errors follow a normal distribution with same variance derived from residues observed
187 for calibration data (Hannouche et al. 2011).

188
189 About sixty grab sample were taken in *Chassieu* site by (Metadier and Bertrand-Krajewski
190 2012) during wet weather conditions between 2002 and 2008 (we have no information on the
191 number of sampled events). For each sample, 25 repeated turbidity measurements and
192 triplicate TSS analysis according to usual standards methods are carried out, including
193 assessment of uncertainties. These have allowed to build a second degree polynomial function
194 ($TSS_{(mg/l)}=12.9+0.7*T_{(FNU)}+7.8e-4*T_{(FNU)}^2$, (Equation 3)) by means of Williamson weighted
195 least squares regression method accounting for uncertainties in both coordinates (TSS and
196 turbidity) A detailed description of this method and uncertainty estimation are reported in
197 (Metadier and Bertrand-Krajewski 2011). The obtained correlation function in *Chassieu* is
198 given in *Figure 1*, (b).

199 Note that the difference in procedure for estimation of TSS concentration at both sites is due
200 to the methods of turbidity measurements and to available TSS-Turbidity data on each site.

201

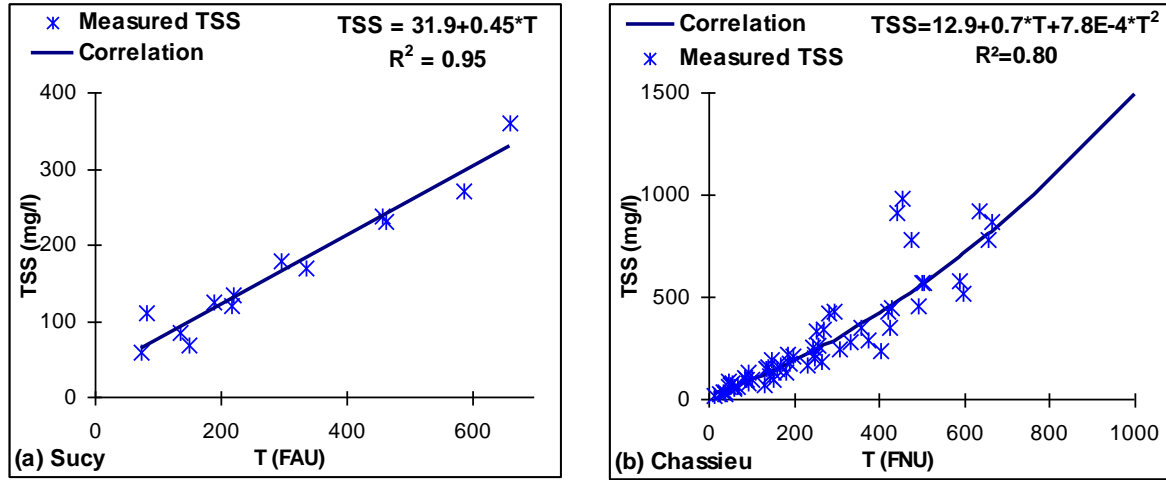


Figure 1: TSS-Turbidity correlation functions: (a) *Sucy* ; (b) *Chassieu*

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The two correlation functions on both sites are different. This may be mainly due to measuring and calculation methods used at each site (attenuation in *Sucy* and nephelometry in *Chassieu*). Indeed, at the *Chassieu* site, this relationship was established by (Metadier and Bertrand-Krajewski 2011) for instantaneous samples with turbidity measured in nephelometry. While on the *Sucy* site, we calculated event mean turbidity for rain events (which are less variable than those of instantaneous turbidities), for which the event mean concentration and turbidity pollutograph are known. Moreover, although the y-intercept (measurement offset) at *Sucy* site is quite high (31.9 mg/l TSS at 0 FAU), its variability at 95% prediction intervals is approximately ± 25 mg/l TSS. It should be noted that this relationship was established for a range of turbidity between 70 and 660 FAU and was used for turbidities varying between 60 and 700 FAU (average value = 250 FAU).

214 CALCULATION METHOD

215 In the case of a discrete sampling of all events for a given year, the pollutant loads M_{pol} for
216 year k could be calculated by sequential summation of loads $M_{j\ pol}$ of all rainfall events
217 (indexed by j with a number N_{events}) that occurred during this year and by sequential
218 summation at time step i (with a number n_j time step), over the duration of each event. It is
219 further assumed that the pollutant load transited during dry weather periods (improper
220 connections, infiltration...) is negligible compared with the one transported during wet
221 weather periods throughout one year. So:

$$222 \quad M_{pol} = \sum_{j=1}^{N_{events}} M_{polj} \approx \sum_{j=1}^{N_{events}} \sum_{i=1}^{n_j} C_{T-polji} \times Q_{ji} \times \Delta t_{ji} \quad (\text{Equation 4})$$

223 With Q_{ji} = flow rate and $C_{T-polji}$ = total (i.e. dissolved and particulate) pollutant concentration
224 at time step i (Δt_{ji}) during the event j . The symbol (\approx) indicates that there is a discretization
225 error.

226
227 Thus, estimating the mass $M_{j\ pol}$ using the above formula requires knowledge of the
228 dynamics of total pollutant concentration C_{T-pol} and flow rate at each time step. Actually, the
229 details of the dynamics of pollutant loads within a rainfall event is not considered by itself,
230 but only as a mean to get an integrated value of the product $Q_{ji} \times C_{T-polji} \times \Delta t_{ji}$ over the

231 duration of the rainfall event. Thus an analysis performed on a flow-weighted composite
232 sample representative of the entire rainfall event j is sufficient for estimating the total
233 pollutant EMC C_{T-pol_j} , and assessing the event load M_{j-pol} of rainfall event j as

234 $M_{j-pol} = C_{T-pol_j} \times V_j$ (Equation 5) with V_j is the volume of water transported during the
235 rainfall j .

236 Continuous monitoring of flow rate is commonly available, and the equation 5 can be applied
237 to events for which monitoring was carried out for providing C_{T-pol_j} . But pollutant
238 concentrations data are always very scarce, due to sampling and analysis constraints. So we
239 investigate the possible combination of continuous monitoring of some parameters with
240 analyses performed on flow rate averaged event mean samples collected from a few rain
241 events. We especially focus on the added value of turbidity monitoring for improving the
242 assessment of pollutant annual load for pollutants which are significantly correlated with TSS
243 EMC.

244
245 In this scope, we distinguish two types of pollutants according to the dependence of their total
246 concentrations on TSS concentration. Indeed, the total pollutant concentration C_{T-pol} is
247 expressed as the sum of dissolved $C_{D-pol}(unit/l)$ and particulate $C_{P-pol}(unit/l)$
248 concentrations ($unit \sim mg$ or μg or ng):

249 $C_{T-pol} = C_{D-pol} + C_{P-pol} = C_{D-pol} + \tau \times TSS$ (Equation 6), with $TSS(mg/l)$ is TSS EMC
250 concentration and τ is the particle pollutant content ($unit/mg$ TSS, i.e. $\tau =$ particulate
251 concentration / TSS concentration = C_{P-pol}/TSS).

252
253 The combination of pollutograph and hydrograph of a rainfall event j allows us to estimate the
254 TSS EMC of this rainfall event using (equations 1, 2 and 3).

255
256 After identifying the rainfall events in a given year (using precipitation and flow rate time
257 series), from one to four stochastic models are used to handle missing data and finally get an
258 assessment of total pollutant EMC for a given pollutant for any event. Then, an annual flow
259 weighted concentration is derived from the EMC values for all events in one particular year,
260 and the process is repeated by the means of Monte-Carlo simulation to derive a mean value
261 and a confidence interval for each considered pollutant.

262 **Model structures**

263 For a given event, two models are used to handle the lack of continuously monitored data:

- 264 1. A precipitation – volume model (model M1) to estimate a value and its uncertainty of
265 the runoff volume of a rainfall event for which there is no flow rate measurement.
- 266 2. A TSS EMC model (model M2) to estimate the TSS EMC probability distribution of a
267 rainfall event for which neither TSS EMC analysis nor turbidity measurements were
268 available (either due to the lack of sensor or to a drift or failure of available sensors).

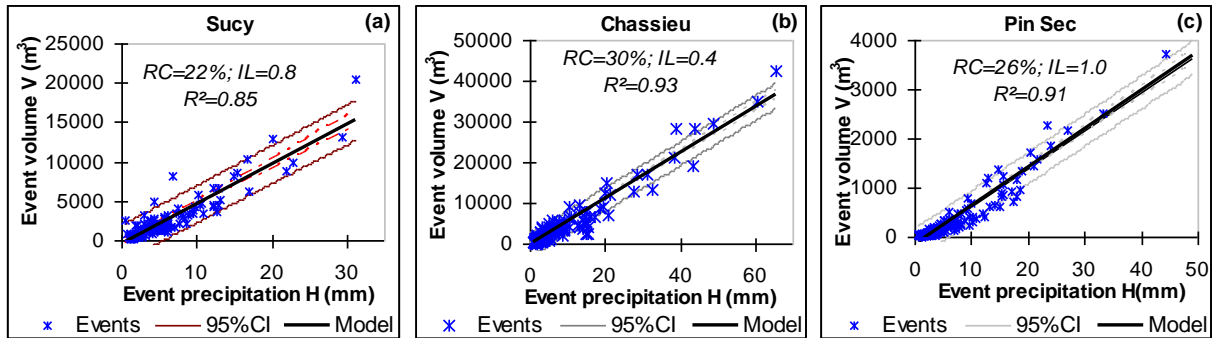
269
270 In addition, two other models are used to extrapolate data from the few events sampled for
271 pollutant EMC analysis to other events, where such analysis is missing:

- 272 3. M3 is used when no correlation between C_{P-pol} EMC and TSS EMC is identified, and
273 C_{T-pol} EMC.
- 274 4. M4 is used when a significant correlation between C_{P-pol} EMC and TSS EMC is
275 identified and provides the probability distribution of C_{T-pol} EMC as the sum of C_{D-pol}

276 EMC overall probability distribution and C_{P-pol} EMC probability distribution assessed
 277 from TSS EMC value and τ .
 278 M2 and M3 models have no input variable and provide an overall distribution whereas M1
 279 and M4 models use a measured variable (rainfall or TSS) as an input in a linear regression,
 280 thus providing a conditional distribution.
 281

282 Precipitation – volume model (Model M1)

283 The first model (M1) is a linear model using the runoff coefficient RC to estimate the event
 284 volume V as a function of the precipitation H according to the relationship
 285 $V = 10 \times A \times RC \times (H - IL)$ where IL is the initial loss (in mm) and A is the catchment
 286 surface area (in ha). For a given catchment, model M1 was fitted by means of least squares
 287 method using all the events for which simultaneous flow rate and rainfall intensity are
 288 available. Figure 2 illustrates the runoff model ($V = 10 \times A \times RC \times (H - IL)$) (Equation 7)
 289 obtained on each site and the corresponding 95% prediction intervals (95% PI). The obtained
 290 runoff coefficients RC are reported in Table 1 above.
 291



292
 293 **Figure 2: Runoff models and corresponding 95% CI (RC= runoff coefficient, IL = initial loss) for: (a)**
 294 **Sucy, (b) Chassieu and (c) Pin Sec**

295 TSS EMC model (Model M2)

296 No model could be identified for linking the TSS EMC for a rainfall event to the
 297 characteristics of this event (precipitation depth, rainfall intensity, preceding dry weather). A
 298 probability distribution model (M2) was used instead and fitted to all TSS measures available
 299 on a given site or derived from turbidity measurements. For a given site, the Kolmogorov-
 300 Smirnov test was used to fit theoretical and TSS EMC empirical distributions at the 5% level.
 301 Different simulations show that the lognormal distribution is well suited for describing the
 302 TSS EMC (KS test, $\alpha=5\%$). Hence, both the mean (m) and standard deviation (SD) of EMCs
 303 (estimated distribution) have been calculated first in natural logarithm space (μ and σ mean
 304 and standard deviation of $(\ln(TSS\ EMC))$) and then transformed into arithmetic space (Romeu
 305 2002) using the formulas: $m = \exp\left(\mu + \frac{\sigma^2}{2}\right)$ and $SD = \sqrt{\exp(\sigma^2) - 1} \times m$ (Equations 8 & 9)
 306 where $\exp(x)$ is the exponential function of x . The parameters of fitted distributions for
 307 different sites are summarized in Table 3.
 308

309 **Table 3: Means and SD of the fitted lognormal distributions of TSS EMC and those of n rainfall events on**
 310 **the three sites Sucy, Chassieu and Pin Sec**

Site	n	μ	σ	m	SD	KS p-value ⁽¹⁾	\overline{EMC} ⁽²⁾	σ_{EMC} ⁽²⁾
Sucy	121	4.83	0.49	141	74	84%	141	73
Chassieu	263	4.63	0.79	140	130	87%	144	144

<i>Pin Sec</i>	18	4.57	0.76	128	114	82%	124	85
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(1) p-value for Kolmogorov-Smirnov test; (2) mean and SD calculated on the n rainfall events

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Note that the TSS EMCs on both *Sucy* and *Chassieu* sites were calculated from the turbidity data, while those of *Pin Sec* site are those of the measurement campaigns (Table 6). Kruskal-Wallis statistical test shows that the distributions of TSS EMCs are not significantly different between the three sites ($\alpha = 5\%$ and p-value=17%). In addition, the same test shows that there is no significant difference between the distribution of TSS EMC from one year to another in the same site (*Sucy* and *Chassieu* sites).

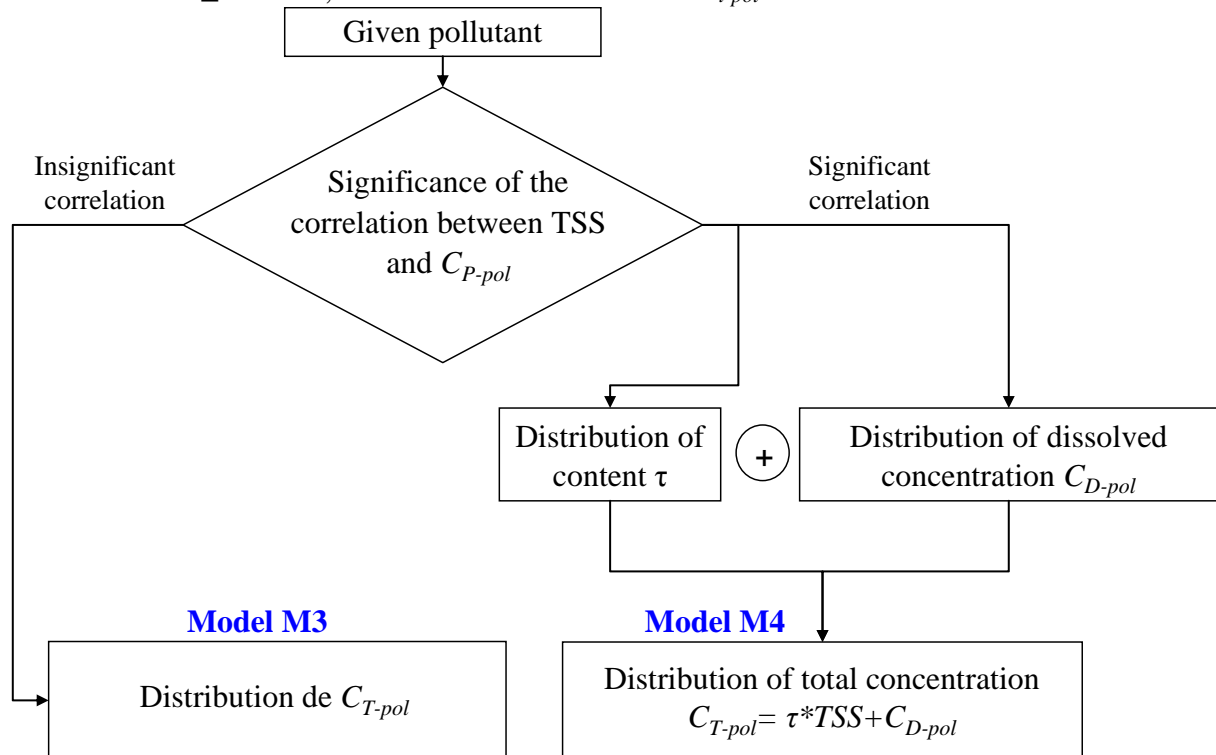
319 C_{T-pol} EMC models (Models M3 and M4)

320 As for TSS, no model was identified for assessing the total pollutant EMC C_{T-pol} according to
321 the characteristics of the corresponding rainfall event. So, a distribution model was applied.
322 Figure 3 illustrates the methodology of calibration of the distribution model of C_{T-pol} EMC.

323

324 First of all, the significance of the correlation coefficient ($\rho_{TSS-pol\ part}$) between TSS EMC and
325 particulate concentration C_{P-pol} EMC was tested for a given pollutant by using Pearson
326 parametric test for normal distribution or Spearman nonparametric test otherwise ($\alpha=5\%$ for
327 all these tests). The significance of this correlation leads the choice between two models:

- 328 1. No significant correlation: a distribution of C_{t-pol} EMC (in $\mu g/l$) (model M3) is used.
329 Model distributions are then fitted, using KS test ($\alpha=5\%$) when the number of events
330 is greater than or equal to 6 (Romeu 2003);
- 331 2. Significant correlation: a model (model M4) is used, which results from a distribution
332 of contents τ (e.g. $\mu g/mg$ TSS), a value of TSS EMC (e.g. mg/l) (obtained by turbidity
333 measurements or M2 model) and a distribution of dissolved concentrations C_{D-pol}
334 EMC (e.g. $\mu g/l$). The distributions of τ and of C_{D-pol} EMC are fitted if the number of
335 events is ≥ 6 . Then, we calculate the total EMC C_{t-pol} .



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Figure 3: Methodology for deriving the distribution model of EMC for a given pollutant

339 Furthermore, the rather low number of sampled rainfall events (*Table 1*) is not practical to fit
340 a distribution of EMC for a given pollutant and a given site, especially in the case of *Chassieu*
341 site (2 to 5 measurements per pollutant, *Table 1*). To solve this problem, the data from all
342 three sites were pooled when no significant site-to-site difference between the EMC
343 distributions of this pollutant was detected. Indeed, the homogeneity of C_{T-pol} EMC for model
344 M3 (or C_{D-pol} EMC or τ for model M4) for a given pollutant between three sites is verified at
345 the level of 5% (ANOVA parametric test if the homogeneity of variance (Levene's test) and
346 normality (Shapiro-Wilk normality test) are accepted, Kruskal-Wallis non-parametric test
347 otherwise (often used as an alternative to the ANOVA where the assumption of normality is
348 not acceptable)). In the case of rejection of the hypothesis of homogeneity of C_{T-pol} (C_{D-pol}
349 EMC or τ), the Siegel–Tukey test of multiple comparisons is applied to find homogeneous
350 groups of sites for a given pollutant. All these statistical tests were performed with the
351 statistical software XLSTAT® (version 2009.3.02, Addinsoft, New York,
352 <http://www.xlstat.com>).

353
354 Kolmogorov-Smirnov test shows that lognormal distributions are well suited to describe
355 pollutants EMCs at the level of 5%: total C_{T-pol} , dissolved C_{d-pol} and particle contents τ (KS p-
356 value $\geq 20\%$). These results are in good agreement with those observed in the literature (EPA
357 2005, Francey et al. 2010, Mourad et al. 2005, Smullen et al. 1999).

358 C_{T-pol} EMC for the different pollutants and groups of pollutants were hence estimated. Indeed,
359 the results for each metal are presented. By contrast, PAHs are presented on the basis of total
360 concentrations, i.e. $\sum_{16} PAH$ (EPA 2005) or $\sum_{13} PAH$ (excluding volatile PAH: N, Acen and
361 Acyl). For PBDE, the results are presented for $\sum_9 PBDE$ and deca-BDE (BDE-209) which
362 displayed the highest concentrations compared to other PBDE. The results of BPA, of
363 octylphenols ($\sum OP$, octylphenol and octylphenol ethoxylates) and nonylphenols ($\sum NP$,
364 nonylphenol and nonylphenol ethoxylates) are also presented.

365
366 Figure 4 and ***Erreur ! Source du renvoi introuvable.*** illustrate in the approach applied for
367 two pollutants: $\sum OP$ and Pb. The method presented above is discussed in both figures.

368 Parameters of the different distributions for models M3 and M4 in natural logarithm space (μ
369 and σ) are reported in *Table 8* in supplementary materials. For more details about the intra
370 and inter-site variability of concentration for a given pollutant, an analysis with a comparison
371 with literature, is detailed in (Gasperi et al. 2014).

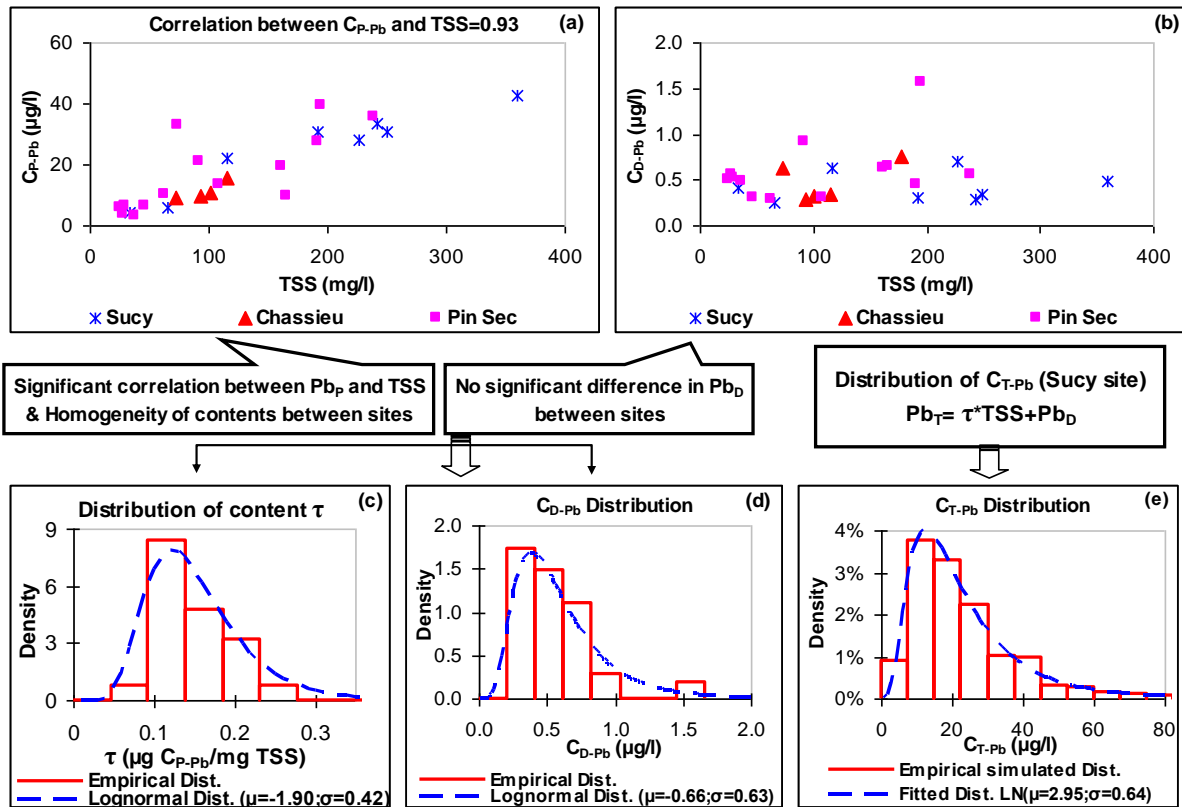


Figure 4: Example of the construction of the model of CT-Pol EMC (M4) for Pb; (e): case of Sucy site

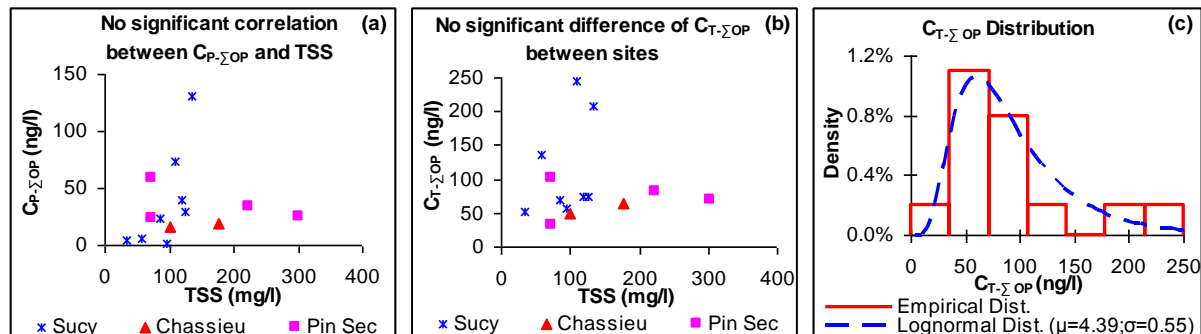


Figure 5: Example of the construction of the model of CT-Pol EMC (M3) for ΣOP

When validated, the lognormal distribution obtained by model M3 is directly used in the calculation of the annual load of this pollutant (example *Erreur ! Source du renvoi introuvable.* c)).

Alternatively, two independent simulations (condition of independence has been checked using the partition coefficient $K_d = \tau/C_{D-pol}$) using obtained lognormal distributions of τ (Figure 4 (c)) and total C_{D-pol} (Figure 4 (d)) for a given pollutant are coupled with a TSS concentration (calculated using turbidity or simulated using model M2) to calculate a C_{T-pol} of this pollutant for the corresponding event (Figure 4 (e)).

Monte Carlo simulations

Monte Carlo simulations are used to combine the different models detailed above for each particular event in a given year and propagate the probability distributions from each model involved for each event to the annual average values and quantify the associated uncertainties. Figure 6 illustrates the methodology for assessing pollutant annual load M_{Pol} for a given year and for a given pollutant using a Monte Carlo simulation (ISO/IEC 2008). Note that the

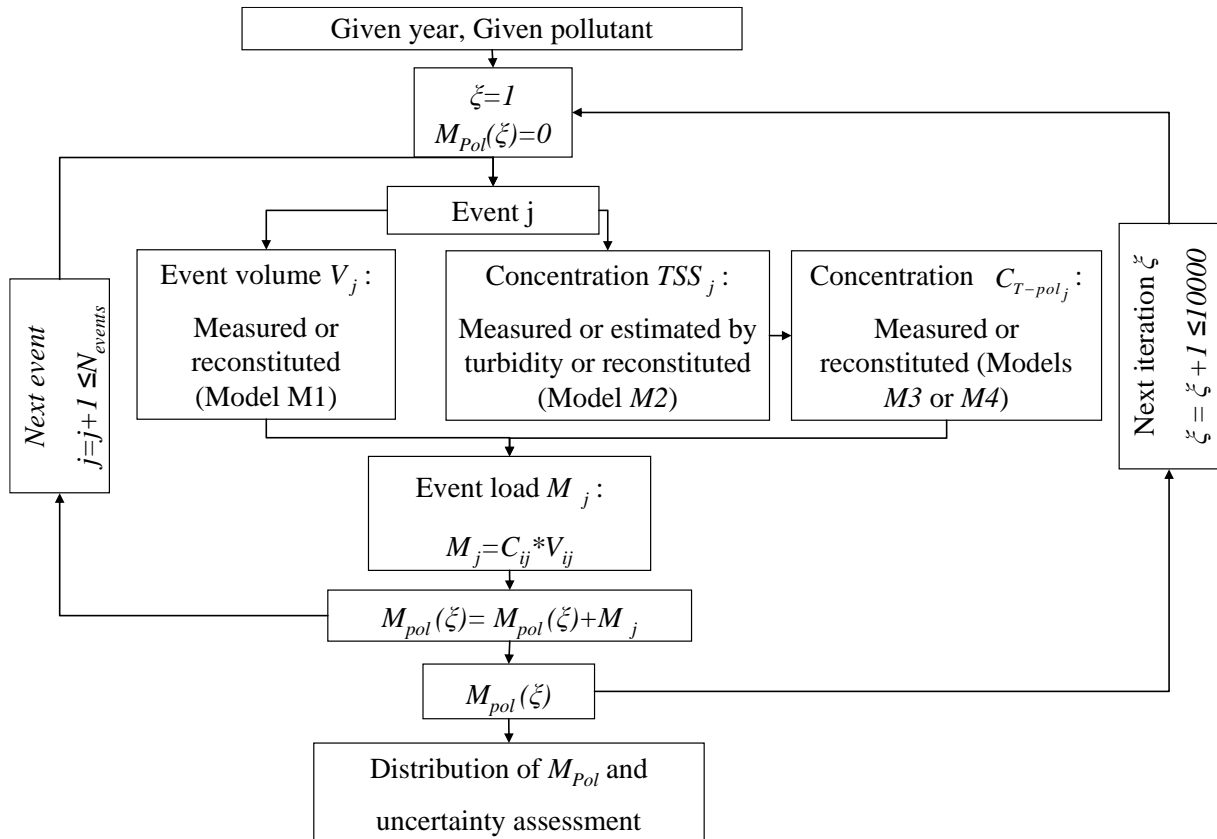
392 hypothesis of independence between the event volume and concentration was checked for
 393 sampled events.

394 Then, the masses of all the events of this year for a given pollutant are summed up. This
 395 process was then reiterated 10,000 times for each year to obtain a probability distribution of
 396 annual load M_{Pol} . The average pollutant annual load and the corresponding uncertainties are
 397 derived from load distribution by using a 95% confidence interval (shortest 95% confidence
 398 interval as recommended by (ISO/IEC 2008) standard).

400 In addition to sources of variability in the models $M2$ to $M4$, various sources of uncertainties
 401 are taken into account in the simulation such as:

- 402 - Measurement uncertainties: the uncertainties in the measured value are assumed to be
 403 normally distributed and independents with their standard uncertainty for:
 - 404 ○ Laboratory analyses: a relative standard deviation (%RSD) equal to 15%
 405 (Gromaire and Chebbo 2001, Ruban et al. 2010);
 - 406 ○ Precipitation depth H_j : a %RSD equal to 10%;
 - 407 ○ Flow rate Q_{ij} : a %RSD equal to 10%;
 - 408 ○ Turbidity: a value of 10 FAU or 10 FNU was used as standard uncertainty
 409 (Lacour et al. 2009, Metadier and Bertrand-Krajewski 2012).
- 410 - Prediction errors of the event volume (Model M1): this one was taken into account using
 411 residual errors implied by the linear model established at a given site. Residual errors are
 412 homoscedastic and normally distributed;
- 413 - Prediction errors of Turbidity-TSS correlation function $f(T)$.

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Figure 6: Methodology for assessing pollutant annual loads

The presented methodology has been implemented in Scilab®-5.4.1 open source software (<http://www.scilab.org>). In the following section, results for TSS and TOC annual loads and those obtained for the different pollutants are discussed. The calculation was performed for 2

421 years in *Sucy* and *Pin Sec* sites (2011 and 2012) and for 5 years in *Chassieu* site (2004 to
 422 2008). To compare the results between the three sites, annual loads for each site are
 423 normalized by active area (act.ha) and they will be called specific annual loads. The active
 424 area S_{act} of a catchment is the area that really contributed to runoff. It was determined by the
 425 area A of each catchment and the average runoff coefficient RC obtained using model M1 (S_{act}
 426 = $RC \cdot Area$, see *Table 1* and *Figure 2*). S_{act} is about 50 ha in *Sucy*, 55 ha in *Chassieu* and 8 ha
 427 in *Pin Sec*.

428 APPLICATION ON THE THREE SITES

429 **Annual precipitations and volumes**

430 At the annual scale, the volumes (\sim net annual precipitation $H_n = (\sum_j H_j - IL)$) expressed in mm
 431 ($\sim 10 \text{ m}^3/\text{act.ha}$) are shown in *Table 4*. The *Chassieu* site has an annual rainfall greater than
 432 that precipitated in *Sucy* and *Pin Sec* sites, which will affect the annual volumes.

433

434

Table 4 : Annual volumes on the three studied sites ($\pm 95\%$ empirical confidence intervals)

Site	Year	Annual volume V_y/S_{act} (mm = $10 \text{ m}^3/\text{act.ha}$)
<i>Sucy</i>	2011	440 ± 10
	2012	525 ± 10
<i>Chassieu</i>	2004	810 ± 15
	2005	580 ± 15
	2006	690 ± 10
	2007	775 ± 10
	2008	840 ± 10
<i>Pin Sec</i>	2011	515 ± 10
	2012	530 ± 10

435 **TSS and TOC annual loads**

436 Specific annual loads of TSS and TOC, for 2 years in *Sucy* and *Pin Sec* sites and for 5 years in
 437 *Chassieu* site are illustrated in *Figure 7(a, b)*.

438 The average values of TSS specific load in *Sucy* and *Pin Sec* sites (between 550 and 700
 439 kg/act.ha/year) are lower than those of the *Chassieu* site (between 700 and 1100
 440 kg/act.ha/year).

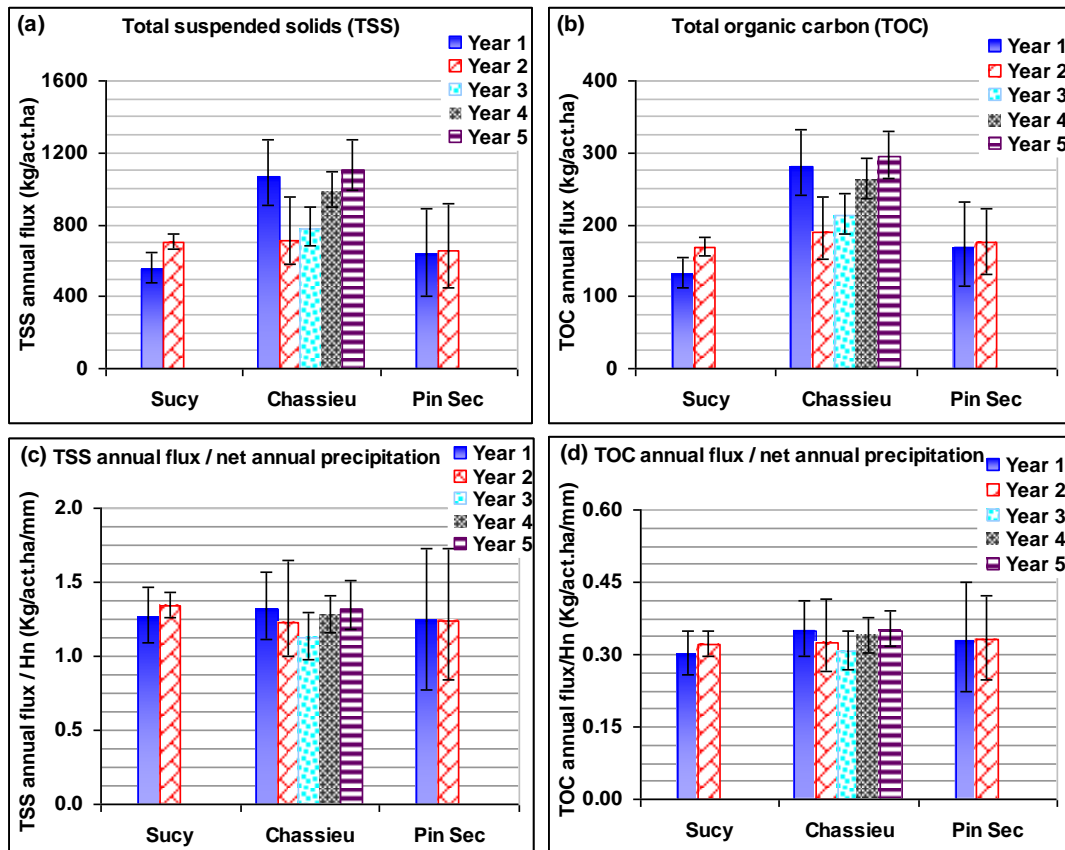


Figure 7: Annual loads at each site (average value from all simulations): (a) TSS annual loads; (b): TOC annual loads; (c) (respectively (d)): TSS (resp. TOC) annual loads per mm of water (net, see Table 4). Error bars represent the 95% empirical confidence intervals

Similarly, the same trend can be observed for TOC specific annual loads (between 130 and 175 kg/act.ha/year in *Sucy* and *Pin Sec* and between 190 and 295 kg/act.ha/year in *Chassieu*). At each site, uncertainties on TSS loads and TOC loads vary from one year to another depending on the amount of available data. This dispersion (around the mean value at 95% CI) varies from 5 to 15% in *Sucy* site, from 10 to 35% in *Chassieu* site and from 30 to 40% in *Pin Sec* site. Indeed, two factors affect the uncertainties of TSS loads on the same site: measurement uncertainties and those caused by selected models due to the absence of measurements. The effect of data reconstitution can be spotted on *Sucy* and *Pin Sec*, where fewer data is available in 2011 than in 2012 from flow rate and/or turbidity monitoring and in *Chassieu* where fewer data is available for 2004 and 2005 than for other years due to failures of the measurement system. In addition, the absence of a turbidity measurement in *Pin Sec* site involves uncertainties on the evaluation of annual loads higher than those observed in *Sucy* and *Chassieu* sites.

For temporal variations, we can observe a low inter-annual variability of TSS load with an apparent influence of meteorological conditions expressed as annual precipitation (Figure 7, (c)). Indeed, the annual load per mm water (net) represents a Site (discharge-weighted) Mean Concentration (SMC). So, the SMC during a given year will be

$$SMC(mg/l) \cong 10^2 \frac{M(kg/act.ha)}{H_n(mm)} \text{ (Equation 10). In other words, the overall TSS SMC is}$$

about 130 ± 15 mg/l in *Sucy*, 125 ± 45 mg/l in *Pin Sec* and 125 ± 20 mg/l in *Chassieu* at a confidence level 95%. TSS SMC uncertainty in *Pin Sec* site is important ($\sim \pm 35\%$) because it is derived from a small number of rainfall events ($n=18$). This latter confirms the results of

467 (Mourad et al. 2005) which stressed that using fewer than 20 sampled rainfall events leads to
468 uncertainties on TSS SMC above 30% (95% half-confidence interval).

469

470 Likewise, the overall TOC SMC is about 31 ± 4 mg/l in *Sucy*, 33 ± 10 mg/l in *Pin Sec* and 33 ± 5
471 mg/l in *Chassieu* at a 95% confidence level.

472 Low uncertainties in SS and TOC SMC in *Sucy* and *Chassieu* sites demonstrates that the use
473 of turbidity monitoring, as indicator of TSS concentration, substantially improves the
474 accuracy of evaluated annual pollutant load.

475 **Annual loads of micropollutants**

476 Annual loads of Pb, \sum OP, \sum_{16} PAH and \sum_9 PBDE per active hectare are shown in *Figure 8*.
477 The loads are presented for *Sucy* and *Pin Sec* sites. For *Chassieu* the PAH and PBDE loads
478 are not calculated, due to limited number of sampled events. The annual loads of all studied
479 pollutants for all years and their overall SMC are shown in *Table 5*.

480 We notice an interannual and intersite variability of annual pollutant loads, as for TSS annual
481 loads. At each site, we observe an interannual variability influenced by meteorological
482 conditions (*Table 4*). The inter-site variability of pollutants annual loads per mm water is
483 logically linked to the calibration of distribution models of pollutants EMCs. Indeed, for
484 pollutant displaying site-to-site differences between *Sucy* and *Pin Sec* sites (\sum_{16} PAH and
485 \sum_9 PBDE (see *Figure 7* and *Figure 8 (c and d)*), pollutants annual loads per mm are different
486 between sites. For example, in spite of similar annual precipitation, the \sum_{16} PAH loads in *Sucy*
487 site are two times higher than those in *Pin Sec* site, but \sum_9 PBDE loads in *Sucy* are ten times
488 lower than those in *Pin Sec*, reflecting local contamination.

489 The Uncertainty on annual loads of different pollutants (at 95% CI) varies between 10 and
490 60%, and may reach 100% as in the case of \sum_9 PBDE in *Pin Sec* site (see *Figure 8 (d)*).
491 Indeed, we can observe two types of the uncertainties of pollutants loads: i) Loads estimated
492 using model M4: (taking into account the correlation between TSS and pollutant
493 concentration for Zn, Cu, Cr, As, Ni, Pb, Sr, V, \sum NP, \sum_{16} PAH (*Sucy*) and \sum_{13} PAH (*Sucy*))
494 have dispersion less than 30% around its average values; ii) By comparison those estimated
495 from model M3 (pollutant uncorrelated with TSS like Cd, Co, Pt, Ti, Mo, BDE-209,
496 \sum_9 PBDE, BPA, \sum OP, \sum_{16} PAH (*Pin Sec*), \sum_{13} PAH (*Pin Sec*)) have dispersion greater than
497 30% around its average values and these uncertainties rise to more than 100% in some cases.
498 This shows the importance of a continuous measurement of turbidity minimizing uncertainties
499 in the estimation of annual loads of pollutants attached to solid particles. This point will be
500 illustrated below to show the importance of considering the correlation between TSS and
501 pollutant particulate concentration in the calculation method.

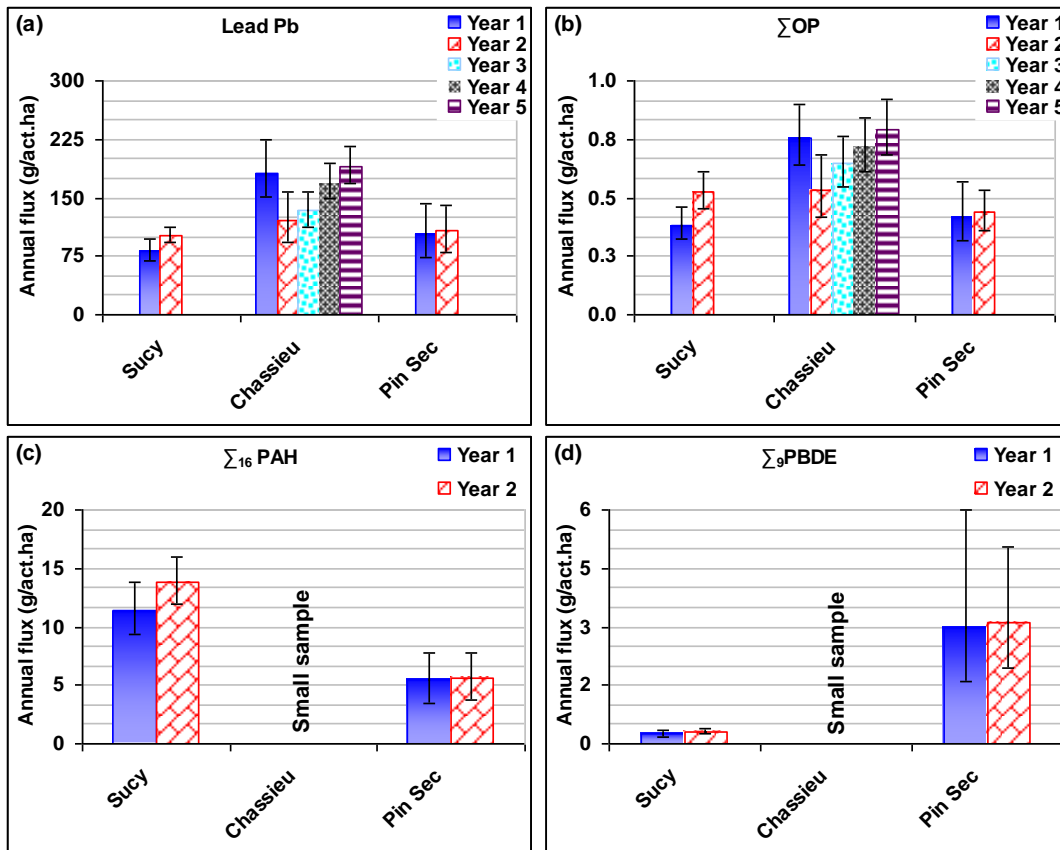


Figure 8: Annual loads at each site of: (a): Lead Pb; (b) sum of Octylphenols Σ OP; (c) sum 16 polycyclic aromatic hydrocarbons Σ_{16} PAH and (d) sum of 9 polybromodiphenylethers Σ_9 PBDE. Error bars represent the 95% empirical confidence intervals. Years 1 and 2: 2011 and 2012 at Sucey & Pin Sec sites, and Years 1 to 5: 2004 to 2008 at Chassieu site.

Efficiency of turbidity monitoring to reduce uncertainties in annual pollutant loads

To illustrate the impact of correlation ρ between $TSS\ EMC$ and $C_{P-Pol}\ EMC$, three cases are simulated and compared for a pollutant having a particulate concentration highly correlated with the concentration of TSS (cases of lead Pb for example, see *Figure 4* and *Figure 8*): i) ρ considered as equal to 0 using model M3; ii) ρ considered with its actual value and using model M4 with TSS analyzed on water samples, iii) ρ considered with its actual value using model M4 with TSS assessed from continuous turbidity measurement. The uncertainties involved by the runoff model M1 can be neglected for comparison purpose: uncertainties obtained by this calculation are due only to errors from models M2 (TSS distribution) and M4 (solute distribution plus TSS correlation).

Figure 9 show that this correlation changes the average annual loads as well as its uncertainties. We don't know the "exact value" of Pb annual load to validate the average Pb annual load obtained for each case. Anyway, the information provided by Pb -TSS correlation lowers the relative uncertainty on the annual concentration, especially if continuous monitoring if turbidity is available. The improvement of the uncertainty observed for case *ii* is explained by the number of events sampled for TSS analysis being larger than the number of events sampled for Pb analysis: 121 rainfall events vs. 24 sampled rainfall events.

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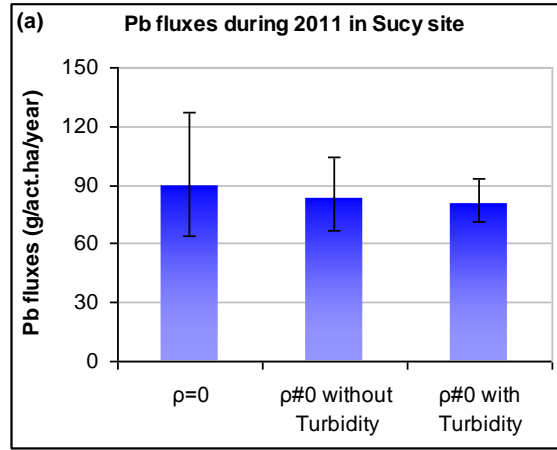


Figure 9: Impact of the correlation between TSS EMC and pollutant particulate EMC with or without turbidity measurements (cases of lead Pb in Sucy site, year 2011)

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Table 5: Annual pollutant load per mm water for all years at each site and overall pollutant SMC. Each interval for pollutant load represents the 95% empirical confidence intervals. The intermediate value is the average value of load. * SMC in µg/l. **NE: No evaluated. * SMC in ng/l**

Load (mg/act.ha/mm)	Pollutant	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Pt	Sr	Ti	V	Zn
Sucy	2011	[12;14;15]	[2;2.6;3.4]	[24;31;40]	[26;31;39]	[280;370;490]	[33;48;68]	[37;43;51]	[160;185;220]	[0.34;0.48;0.67]	[920;1085;1285]	[185;245;330]	[38;43;50]	[1530;1800;2120]
	2012	[14;15;16]	[2.3;2.8;3.4]	[28;33;40]	[30;33;36]	[330;380;450]	[40;54;74]	[42;47;53]	[180;195;215]	[0.42;0.54;0.72]	[1070;1220;1400]	[215;255;305]	[43;47;51]	[1760;1920;2110]
	SMC*	1.4 ± 0.1	0.27± 0.04	3.2 ± 0.5	3.2 ± 0.4	38 ± 6	5.1 ± 1.4	4.5 ± 0.4	19 ± 2	0.05 ± 0.01	116 ± 12	25 ± 4	4.5 ± 0.4	187 ± 16
Pin Sec	2011	[39;45;53]	[1.9;2.8;4.2]	[23;33;49]	[27;34;44]	[290;410;600]	[26;44;80]	[35;44;57]	[145;205;275]	[0.27;0.45;0.77]	[250;330;430]	[190;270;400]	[38;45;55]	[1590;1920;2360]
	2012	[41;46;51]	[2.2;2.8;3.7]	[26;33;43]	[30;35;41]	[325;413;535]	[31;45;67]	[38;44;53]	[150;200;265]	[0.32;0.45;0.65]	[275;330;395]	[215;270;355]	[40;46;52]	[1710;1940;2220]
	SMC*	4.6 ± 0.4	0.28± 0.06	3.3 ± 0.7	3.4 ± 0.8	41 ± 10	4.5 ± 1.7	4.4 ± 0.9	20 ± 4	0.05 ± 0.02	33 ± 6	27 ± 7	4.5 ± 0.5	193 ± 28
Chassieu	2004	[12;15;17]	[2.1;3;3.6]	[26;35;43]	NE**	[295;440;540]	NE**	[39;49;57]	[160;225;280]	[0.32;0.51;0.65]	[950;1220;1430]	[195;290;355]	[41;50;57]	[1710;2050;2340]
	2005	[10;14;16]	[1.5;2.8;3.6]	[19;33;42]		[210;410;520]		[32;47;57]	[110;210;270]	[0.23;0.5;0.66]	[770;1150;1400]	[140;270;350]	[34;47;56]	[1400;1940;2310]
	2006	[11;13;15]	[2;2.7;3.2]	[24;31;38]		[275;375;460]		[36;45;52]	[150;190;220]	[0.33;0.51;0.65]	[890;1095;1265]	[180;250;300]	[38;44;50]	[1570;1830;2050]
	2007	[13;14;16]	[2.2;2.9;3.4]	[26;34;41]		[330;425;495]		[38;48;55]	[180;220;240]	[0.33;0.51;0.64]	[975;1185;1360]	[215;280;330]	[43;49;54]	[1760;2000;2200]
	2008	[13;15;16]	[2.3;3;3.5]	[27;36;42]		[340;440;515]		[41;49;56]	[180;225;250]	[0.34;0.52;0.64]	[1020;1225;1400]	[220;290;345]	[44;50;56]	[1820;2070;2280]
	SMC*	1.4 ± 0.1	0.29± 0.03	3.4 ± 0.4				42 ± 5		4.8 ± 0.4	21 ± 2	0.05 ± 0.01	118 ± 10	28 ± 3

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Load (mg/act.ha/mm)	Pollutant	∑ ₁₆ PAH	∑ ₁₃ PAH	BDE-209	∑ ₉ PBDE	BPA	∑OP	∑NP
Sucy	2011	[20;26;32]	[20;24;31]	[0.38;0.55;0.8]	[0.41;0.58;0.83]	[3.7;4.6;5.6]	[0.73;0.87;1.05]	[10;12;15]
	2012	[22;26;31]	[22;24;29]	[0.45;0.58;0.74]	[0.48;0.6;0.77]	[4.4;5.2;6.2]	[0.86;1;1.16]	[11;13;15]
	SMC***	2600 ± 400	2400 ± 350	57 ± 10	59 ± 12	490 ± 65	95 ± 10	1240 ± 150
Pin Sec	2011	[9;11;13]	[7;9;10]	[0.31;0.58;1.17]	[0.3;0.58;1.21]	[3.1;4.2;6]	[0.61;0.81;1.11]	[9;12;16]
	2012	[9;11;12]	[8;9;10]	[0.37;0.59;0.99]	[0.37;0.59;0.97]	[3.5;4.3;5.4]	[0.68;0.82;1.01]	[10;12;15]
	SMC***	1060 ± 120	875 ± 100	58 ± 33	58 ± 35	430 ± 90	80 ± 15	1190 ± 250
Chassieu	2004	NE**	NE**	NE**	NE**	[4;4.9;5.9]	[0.79;0.93;1.11]	[10;13;15]
	2005					[3.2;4.8;5.8]	[0.65;0.92;1.1]	[8;12;15]
	2006					[3.9;4.9;5.7]	[0.76;0.93;1.07]	[10;12;14]
	2007					[3.8;4.8;5.7]	[0.77;0.93;1.06]	[10;12;14]
	2008					[4;4.9;5.7]	[0.79;0.94;1.08]	[11;13;15]
	SMC***					490 ± 50	95 ± 10	1240 ± 110

532 **CONCLUSIONS**

533 A method was developed to set up annual pollutant loads and its uncertainties using a large
534 dataset of pollutant EMC and continuous turbidity, flow rate and rainfall intensity recordings.
535 This stochastic method is original and allows the coupling between a few event sampling
536 campaigns and continuous measurements of hydrological and water quality parameters
537 (rainfall intensity, flow rate, turbidity).

538 The results obtained can be summarized as follows:

- 539 - Lognormal distributions are well suited to describe pollutant EMC;
- 540 - The inter-annual variability of the pollutant annual loads in a given site are mainly
541 influenced by weather conditions (annual precipitation);
- 542 - The inter-site variability of the pollutant annual loads per mm of water is related to the
543 distribution of EMC of target pollutant.
- 544 - Annual loads of pollutants can be estimated with uncertainties ranging from 10% to 60%
545 and can reach 100% for some pollutants. For the pollutants with a particulate fraction not
546 correlated to TSS concentrations, the dispersion is greater than 30%. For the pollutants
547 highly correlated with TSS concentration, this dispersion can be significantly reduced
548 (10% to 30%) if we have information about TSS concentration (continuous measurement
549 of turbidity).

550 A continuous measurement of turbidity can improve the estimation of annual loads of some
551 pollutants attached to solid particles. Such results can be used to identify priority sources of
552 pollution and then direct preventive / curative actions.

553 It would be worthwhile to pursue this line of research at other sites as a preliminary step to
554 generalization.

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644 SUPPLEMENTARY MATERIALS

645 **Table 6: General characteristics of sampled rainfall events followed by a laboratory analysis in the three**
646 **studied sites (min-max and median values) (Gasperi et al. 2014)**

	H ¹ (mm)	Duration (h)	I _{mean} (mm.h ⁻¹)	I _{max} ² (mm.h ⁻¹)	PDWP ³ (d)
<i>Sucy</i> (n=24)	1.2-38.6 8.43	0.6-26.3 7.9	0.4-3.8 1.5	2.4-24 7.9	0.17-9.18 2.1
<i>Chassieu</i> (n=7)	2.4-50.0 18.8	3.1-31.6 14.5	0.8-1.7 1.2	4.7-22.7 12.2	0.2-9.8 2.8
<i>Pin Sec</i> (n=18)	2.3-49.9 15.4	2.7-60.5 19.2	0.3-4.0 0.8	2.4-28.8 11.4	0.19-22.29 2.60

648 1) Precipitation depth; 2) I_{max} evaluated over 5-min intervals; 3) Preceding dry weather period, in days. Min-Max
649 values, as well as median values;
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651 **Table 7: Pollutants analyzed and number of rainfall events (Gasperi et al. 2014)**

Groups (n=46)	Number of rainfall events	Substances and abbreviations
Metals (n=13)	Sucy: 8	Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), Zinc (Zn), Platinum (Pt), Vanadium (V), Cobalt (Co), Molybdenum (Mo), Strontium (Sr), Titan (Ti)
	Pin Sec: 15	
	Chassieu: 5	
PAH (n=16)	Sucy: 8	Naphthalene (N), Acenaphthylene (Acyl), Acenaphthene (Acen), Fluorene (F), Phenanthrene (P), Anthracene (A), Fluoranthene (Fluo), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(cd)pyrene (IP), Dibenzo(ah)anthracene (DahA), Benzo(ghi)perylene (BPer)
	Pin Sec: 7	
	Chassieu: 4	
PBDE (n=9)	Sucy: 12	BDE-28 [tri], BDE-47 [tetra], BDE-99 [penta], BDE-100 [penta], BDE-153 [hexa], BDE-154 [hexa], BDE-183 [hepta], BDE-205 [octa], BDE-209 [deca]
	Pin Sec: 7	
	Chassieu: 2	
Bisphenol A and APnEOs (n=1+7)	Sucy: 12	Bisphenol A (BPA) Nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), nonylphenol monocarboxylate (NP1EC), 4-tert-octylphenol (OP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO)
	Pin Sec: 7	
	Chassieu: 2	

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Table 8: Parameters of distributions in natural logarithm space (μ and σ) for models M3 (C_{T-pol} distribution) and M4 ($C_{D-pol} + \tau$ distributionS). See equations 9 and 10 to switch from the logarithmic space to arithmetic space (m and SD). Note: The units are given in the arithmetic space

Model M3 : C_{T-pol} (unit)						Model M4: ξ (unit*/mg TSS) and C_{d-pol} (unit)																
Substance	Sucy		Chassieu		Pin Sec		Substance	τ and C_d	Sucy		Chassieu		Pin Sec									
	μ	σ	μ	σ	μ	σ			μ	σ	μ	σ	μ	σ								
Cd ($\mu\text{g/l}$)	-	0.81	pooled with Sucy *				TOC (mg/l)	τ	1.58	0.21	pooled with Sucy											
Co ($\mu\text{g/l}$)	0.95	0.77						C_{d-pol}	1.53	0.75												
Pt ($\mu\text{g/l}$)	-	0.92					τ	0.42	0.26													
Ti ($\mu\text{g/l}$)	2.98	0.84					C_{d-pol}	3.82	0.43													
Mo ($\mu\text{g/l}$)	1.15	0.98	Small sample: not processed				Cu ($\mu\text{g/l}$)	τ	-1.28	0.43	Small sample: not processed											
\sum_{16} PAH (ng/l)	M3 not relevant: \rightarrow M4							6.90	0.47	C_{d-pol}					1.58	0.55	τ	-3.52	0.27	M4 not relevant \rightarrow M3		
\sum_{13} PAH (ng/l)							6.70	0.48	C_{d-pol}	-1.21					0.52	τ	3.00	0.52				
BDE-209 (ng/l)	3.70	0.99					5.47	1.40	C_{d-pol}	5.42					0.63	C_{d-pol}	5.42	0.63	3.85 0.58 0.78 0.37			
\sum_9 PBDE (ng/l)	3.64	1.00					5.48	1.39	C_{d-pol}	4.81					0.60	τ	-4.74	0.20				
BPA (ng/l)	6.00	0.62					pooled with Sucy	pooled with Sucy							Pb ($\mu\text{g/l}$)	τ	-1.90	0.42	pooled with Sucy			
																C_{d-pol}	-0.66	0.63				
\sum OP (ng/l)	4.39	0.55													Sr ($\mu\text{g/l}$)	τ	-1.91	0.43				
																C_{d-pol}	4.38	0.60				
															V ($\mu\text{g/l}$)	τ	-3.28	0.33				
							\sum NP (ng/l)	C_{d-pol}	0.31	0.49												
								τ	0.76	0.20												
								C_{d-pol}	6.45	0.65												

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